

# Influence of Grain size on the Electrical Properties of $\text{Sb}_2\text{Te}_3$ Polycrystalline Films.

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Resistance of vacuum deposited  $\text{Sb}_2\text{Te}_3$  films of thickness between 100-500nm has been measured in vacuum. It is found that the resistance of the polycrystalline films strongly depends on the grain size and inter-granular voids. The charge carrier are shown to cross this high resistivity inter- granular void by ohmic conduction. The barrier height as well as temperature coefficient of resistance are also shown to depend on the grain size and inter- grain voids.

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## I. INTRODUCTION

The transport mechanism and in turn the cause of resistance is of fundamental importance. Various model, especially for thin films, exist to understand the contribution from different scattering mechanisms. The film resistance, however, may be due to a combination of three mechanisms, namely (i) due to scattering from phonons, impurities and point defects etc., (ii) from film surface and (iii) due to grain boundaries which would be predominant in polycrystalline films<sup>1</sup>. Different models exist to explain the dependence of resistance on film thickness. In the case of scattering from the film surface the variation from film resistivity with film thickness was given by the Fuchs- Sondheimer (F-S) relationship<sup>2</sup>

$$\rho(d) = \rho_o \left[ 1 + \frac{l_g}{d}(1 - p) \right]$$

Where  $l_g$  is the mean free path, 'd' is the film thickness and  $\rho_o$  the resistivity of the bulk sample. The constant 'p' indicates the fraction of electrons being reflected from the surface. The value indicates the scattering mechanism, for example p=1 indicates specular reflection. A similar relationship was established by Mayadas and Shatzkes (M-S)<sup>3</sup> to explain the scattering from grain boundaries, with a very similar functional dependence with film thickness. However, the model is limited to very thin films with an added restriction that the grain size are of the order of film thickness. The grain boundary is defined as region between two grains where crystal orientation changes. The transport properties of  $\text{Sb}_2\text{Te}_3$  films like resistivity, Hall coefficient, mobility and Seeback coefficient have been extensively studied<sup>4,5,6,7,8</sup>, and reports in literature indicate films to be p-type with narrow band gap. However, all these reports are silent on the mechanism of scattering and in turn the source of resistivity. Only Damodara Das et al<sup>7</sup> have reported resistivity as a function of thickness ( $50\text{nm} < d < 120\text{nm}$ ). The article states average grain size to be of the order of film thickness and indicates the scattering mechanism to be that of grain boundary scattering in

accordance to the M-S model. However, no report exists on the variation of resistance or resistivity of  $\text{Sb}_2\text{Te}_3$  films with grain size in thicker films. This article investigates variation of resistance in films whose thickness is enough to assume that the variation in resistivity is independent of defects and specular scattering.

## II. EXPERIMENTAL

Films of  $\text{Sb}_2\text{Te}_3$  were grown on glass substrates kept at room temperature, using thermal evaporation method.  $\text{Sb}_2\text{Te}_3$  ingot of high purity (99.99%) supplied by Aldrich (USA) were used as the starting material. The crushed ingot were evaporated from molybdenum boat at a vacuum better than  $10^{-6}$ Torr. The film thickness was measured using Dektak IIA surface profiler. The movement of the mechanical stylus across the edge of the film determines the step height or the films thickness. Indium contacts were grown on the glass substrates before they were placed in the chamber, such that a strip of  $\text{Sb}_2\text{Te}_3$  film of dimensions  $2.3\text{cm} \times 1.65\text{mm}$  could be fabricated on these contacts using a mask. The I-V characteristics of the films were measured by four probe method. It was found to be linear between 25mV-24V, showing the ohmic nature of indium contacts as well as the polycrystalline film for applied field. The films' resistance were measured by an high input impedance digital multimeter. The structural and compositional analysis of these films were done using Phillips PW1840 X-ray diffractometer and Shimadzu ESCA750 (Electron Spectroscopy for Chemical Analysis). The films were found to be stoichiometrically uniform over the area 5cm x 5cm as determined by ESCA carried out in various regions of the film. The morphological analysis was done with JOEL 840 Scanning Electron Microscope (SEM). The as grown films showed tendency of ageing<sup>9</sup>, where the resistance of the film varied with time and saturated to a constant value in couple of weeks. The results presented in this article are of films which had achieved such saturation.

## III. RESULTS AND DISCUSSION

### A. Variation Resistance with grain size

The average grain size was determined from both SEM micrographs and X-ray diffractograms. The grain size was calculated using the Full Width at Half Maxima (FWHM) of X-Ray peaks<sup>10</sup>. The results of grain size found by both methods were in agreement. A plot between the film thickness and grain size shows no trend (fig 1). This variation in grain size with film thickness may be a result of not having perfectly identical conditions during film evaporation. It also represents the randomness of the growth process. This shows that the average grain size is not proportional to the film thickness and resistance or resistivity will have to be studied both as a function of thickness and grain size to resolve the main contributor in scattering mechanism. The F-S theory shows that the contributions from the surface leads to an inverse proportionality with thickness (equation 1), where the model is restricted to cases where the charge

carriers mean free path is of the order of the film thickness ( $l_g \sim d$ ). However, since the samples in our study have thickness between 130-500nm, the film thickness is far greater than the mean free path. Beyond this limit one can assume the films resistivity to be same as that of the bulk, showing no further change with increasing film thickness. Thus, film's resistance in this limit should only fall inversely with thickness. Figure 2 shows the resistance of aged  $\text{Sb}_2\text{Te}_3$  films falling linearly with increasing thickness. It can be understood trivially, that for the resistance of the film to vary linearly with thickness as shown in figure 2, the resistivity would have to show a parabolic relationship with film thickness. Another important contributor to resistance is the grain boundary. However, that too requires an inverse proportionality with thickness. This lack of trend may be due to the assumption in M-S theory that the grain size is proportional to the film thickness, which is not the case here. It is clear that in the present study the surface scattering and grain boundary scattering do not contribute to the film resistance. Hence, to investigate the influence of the grain size on transport properties, variation of resistance with grain size was studied. Figure 3 shows the variation of film resistance with grain size. As stated earlier the average grain size was determined from both SEM micrographs and X-ray diffractograms. The grain boundary is defined as region between two grains where crystal orientation changes. The representative micrographs of  $\text{Sb}_2\text{Te}_3$  in figure 4 however, show large distances between two grains. The grains tend to have the resistivity of the bulk, however, even if there is an inter-connectivity between two neighbouring grains this region will have high resistivity by purely geometry of narrowing<sup>11</sup>. These voids, hence would definitely contribute differently from the defined grain boundary in M-S theory.

Volger's model<sup>12</sup> assumes the film to be made up of cubical grains of edge size 'a' arranged in an ordered manner, as shown in fig. 5a, with equal spacing between the neighbouring grains. The inter-grain distances are different along x, y and z directions and are same along any one direction. Consider the film has 'q' number of grains arranged regularly at equal inter-grain spacing ' $t'_x$ ' along the length 'l' and 'r' and 'p' grains arranged along the width and thickness of the film. Also, the resistance is measured along the length of the film by taking the contacts across the cross-section in the yz plane, then the points A-B, C-D etc. shown in fig. 5a are at equal potential. The equivalent dc circuit of this arrangement of measurement would be as shown in figure 5b, where ' $R'_b$ ' represents the high resistance of the inter-grain voids<sup>13,14,15</sup>. As can be seen in figure 5b, the whole film can be considered to be a parallel combination of 'pr' resistive elements, where resistance of each element is given by<sup>11,16,17</sup>

$$R_1 = qR_g + (q - 1)R_b$$

Thus, the net resistance along the length of the film between the two contacts would be given as

$$R_{net} = \frac{qR_g + (q - 1)R_b}{pr}$$

Seto<sup>18</sup> made a similar simplification step by assuming the problem to be that of one dimension. ' $R'_b$ ', the high resistance of the inter-grain voids, is a function of ' $t'_x$ ' which in turn would depend on the mechanism by which charge carriers would cross the inter-grain boundary. Many suggestions have been made for explaining the cross over, such

as ohmic conduction, tunnelling or thermionic emission<sup>19</sup>. It may also be a combination of these, depending on the actual inter-grain distances. The resistance of such a film, assuming ohmic conduction in between grains is given as<sup>20</sup>

$$R_{net} = \alpha \frac{1 + kx}{(1 + x)^2} \quad (1)$$

where  $\alpha$  is a proportionality constant, given as

$$\alpha = \frac{\rho_g l^2}{V - V_{void}}$$

In true sense  $\alpha$  is not a constant since  $V_{void}$  will depend on the grain size, as also film dimensions, including its thickness. However,  $V_{void}$  is assumed to be a slow varying function of film thickness, or constant. The constant 'k' represents a ratio of the inter-grain region's resistivity to the grain's resistivity. Since the void resistivity is large, 'k' obviously is a very large entity. The variable is a ratio of the inter-grain length and the grain edge or

$$x = \frac{t_x}{a}$$

where 'a' is the grain size, assuming as in Volger's model, the grains to be cubic in nature. The inter-grain distance, 't<sub>x</sub>' is extent of void in 'x' direction (along length of the film strip), since the resistance is measured along the length of the film. The inter-grain distance varies as a function of the grain size depending the mechanism of grain growth. Since, the Sb<sub>2</sub>Te<sub>3</sub> films aged to a hexagonal crystal state, with  $c \gg a$ , it should show easier grain growth along the length and width as compared with that along restrictive film thickness. The films hence aged with the c-axis aligned normal to the substrate plane<sup>20</sup>. As per Volger's model 'q', the grain number along the length, would be decreasing more rapidly than 'p', that along the film's thickness, leading to a general trend of decrease in resistance. Thus, the variation of inter-grain distance with grain size for the films in consideration would be given as<sup>20</sup>

$$t_x = a \left( \frac{pra^2l - \Delta V}{\Delta V - pra^3} \right) \quad (2)$$

where  $\Delta V = V - V_{void}$ . Thus, it can be seen that the variable, is a function of the grain size, 'a'. The increase in void size with increasing grain size can be appreciated from the representative SEM micrographs. Equation 2, is physically valid for positive values, which requires

$$pra^2l > \Delta V > pra^3$$

Considering an extreme case of  $pra^2l \gg \Delta V \gg pra^3$  along with the stated assumption that  $\Delta V$  is constant, then equation 2 may be written as

$$t_x = a \left( \frac{pra^2l}{\Delta V} \right)$$

The variable 'x' required for equation (1) can then be expressed as

$$x = \frac{t_x}{a} = a^2 \left( \frac{prl}{\Delta V} \right) = \beta a^2 \quad (3)$$

This increase in inter-grain distance with growing grain size was discussed in our earlier work<sup>20</sup>. Hence, using equation (3) the films resistance given by equation (1), can be expressed as

$$R_{net} = \alpha \frac{1 + k\beta a^2}{(1 + \beta a^2)^2} \quad (4)$$

Equation (4) fits quite well to the experimental observations as shown by the solid line in figure 4. The values of the constants evaluated by fitting are  $\alpha = 2308 \Omega$ ,  $\beta = 20.44 \times 10^{-6} \text{\AA}^2$  and  $k \sim 54$ . As stated earlier, the constant  $k$  is a ratio of the high resistivity of the inter-grain region as to the low resistivity of the grains. The numerical value shows the resistivity of the inter-grain region will be nearly  $10^2$  times that of the low resistivity region, which is consistent with the with the assumption that inter-grain region can be assumed to be a path of high resistance.

### B. Variation of Barrier Height with grain size

The voids between neighbouring grains would present itself as a barrier which the charge carriers would have to transverse to establish current flow. The magnitude of the barrier height can be computed from the slope of the plot between  $\ln(\sigma)$  and temperature inverse ( $1/T$  in Kelvin). The barrier height was calculated using this method for various film thickness. The variation is shown in figure 6. The variation in barrier height with film thickness maybe due to one or a cumulative effect of the following (i) variation in the grain size of the polycrystalline film, (ii) a large density of dislocations, (iii) quantum size effects and (iv) change in film stoichiometry. Since the film thickness of this study is large the quantum size effect is immediately ruled out. Careful growth technique followed by ageing would minimise the contribution due to dislocation and off stoichiometric compositions, however, can not be completely ruled out. The major contribution hence would be due to the size of the grains. Slater<sup>21</sup> estimated the barrier height as a function of grain size by modelling grain boundary as a pn type of structure. The variation is given as

$$E_b = E_o + \frac{N_o e^2}{4k\epsilon_o} \left( t_x - \frac{N}{N_o} a \right)^2 \quad (5)$$

where  $N_o$  is the doping concentration,  $N$  the carrier concentration,  $k$  the dielectric constant of the material. The barrier height increases with grain size for  $N_a/N_o > t_x$ , which would be the case in pure samples ( $N > N_o$ ). A fit for the experimental data using equation 3, which states that the barrier width in proportional to the square of the grain size, along with the estimated proportionality constant (b) and equation 5 is shown by the continuous line in figure 6. The fit shows reasonable agreement, however it does indicate possible contributions from dislocations etc. The values of the coefficients of equation 5 are  $E_o = 5.66 \text{ meV}$ ,  $N/N_o = 90$  and  $N_o e^2 / 4k\epsilon_o = 2.65 \times 10^{-9} \text{ meV} - \text{\AA}^2$ . The ratio of  $N/N_o$  may appear to be very small, however, it should be noted that the curve fitting was done using the earlier estimated proportionality constant ( $\beta$ ). Thus, the influence of the inter-grain voids and grain size on the magnitude of barrier height and various characterising parameters of the film is evident. This though expected is different from an

earlier study by Rajagopalan et al<sup>4</sup> on films of  $\text{Sb}_2\text{Te}_3$  with thickness between 160nm and 800nm which reported that the barrier height was independent of the film thickness. In the next section we investigate the role of the inter-grain voids on another parameter used to characterise the transport properties of a material.

### C. Temperature coefficient of Resistance

The resistance of the film is a function of temperature. The variation of resistance with temperature in general is expressed as

$$R = R_o(1 + \frac{\alpha}{R_o}T)$$

Thus the temperature coefficient of resistance or TCR<sup>22</sup> is given as

$$\frac{1}{R_o} \frac{dR}{dT} = \frac{\alpha}{R_o} \quad (6)$$

While TCR is positive for metals, it is negative in case of semiconductors. The F-S model for very thin films states that the variation of TCR with film thickness follows an identical form as expressed by equation (1). However, there seems to be no model in the literature to explain the variation of TCR with either film thickness or grain size for films with thickness greater than the mean free path of their charge carriers. A plot between TCR and grain size seems scattered (not shown). However, the plot between TCR and barrier height is a straight line, figure 7, with slope  $-8.6 \times 10^{-5}(\text{°C} - \text{meV})^{-1}$  and intercept  $-2.66 \times 10^{-5}(\text{°C}^{-1})$ . It immediately follows from the linearity between TCR and  $E_b$  along with equation (5) that the TCR would be a polynomial function of the grain size. This explains the seemingly scattered data points of TCR with grain size as discussed. It also explains the lack of any model or theory on the variation of TCR with grain size. The relationship shows that with increasing barrier height, the rate of change of resistance with temperature ( $dR/dT$  or TCR, equation 6) becomes increasingly smaller. The negative temperature coefficient of resistance in semiconductors is a result of increasing charge carriers due to breaking covalent bonds. An increased barrier height implies it's more difficult for the charge carriers to escape into the voids from the grains, confining the increased number of carriers inside the grain itself. This rapidly brings down the resistance of the grain contributing to a negative TCR proportional to the barrier height.

## IV. CONCLUSIONS

The dc transport properties of  $\text{Sb}_2\text{Te}_3$  films with thickness between 130-500nm have been discussed. The properties showed no size effects as was expected, since the film thickness was far greater than the charge carriers mean free path. The films resistance, the barrier height and temperature coefficient of resistance (TCR) showed a strong dependence

on both the grain size and inter- grain void. The inter-grain void was approximated to vary with increasing grain size, enabling to study the above properties of the films as a function of grain size.

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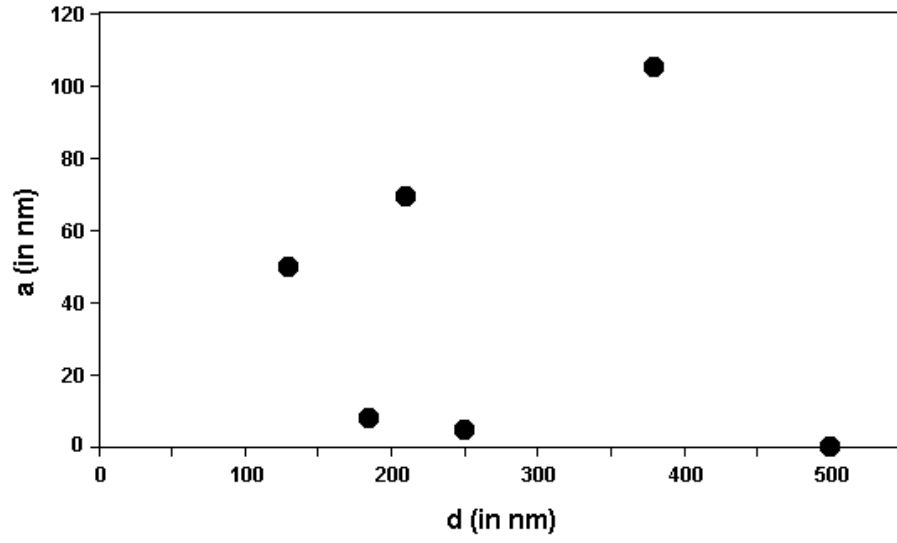


FIG. 1: The variation of grain size in the polycrystalline films for various thickness of  $\text{Sb}_2\text{Te}_3$  grown by thermal evaporation method, show no trend.

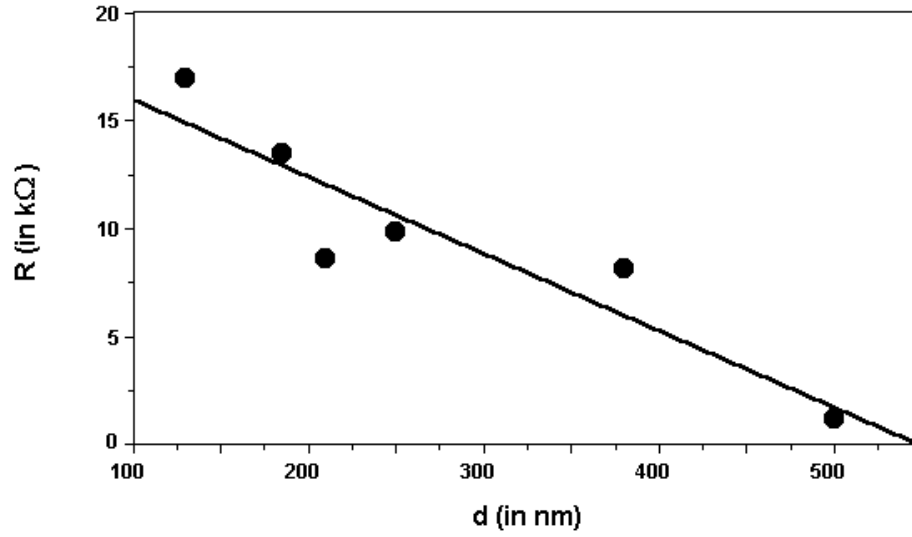


FIG. 2: Variation of film resistance with film thickness of various polycrystalline  $\text{Sb}_2\text{Te}_3$  films after they have completely aged.

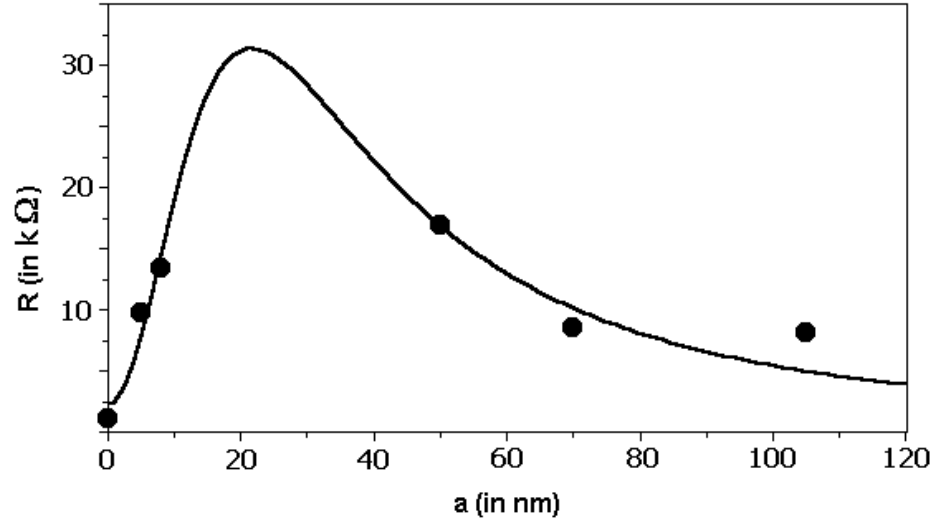


FIG. 3: Variation of film resistance with grain size of various polycrystalline  $Sb_2Te_3$  films. The continuous curve is a fit of the experimental points using equation (4).

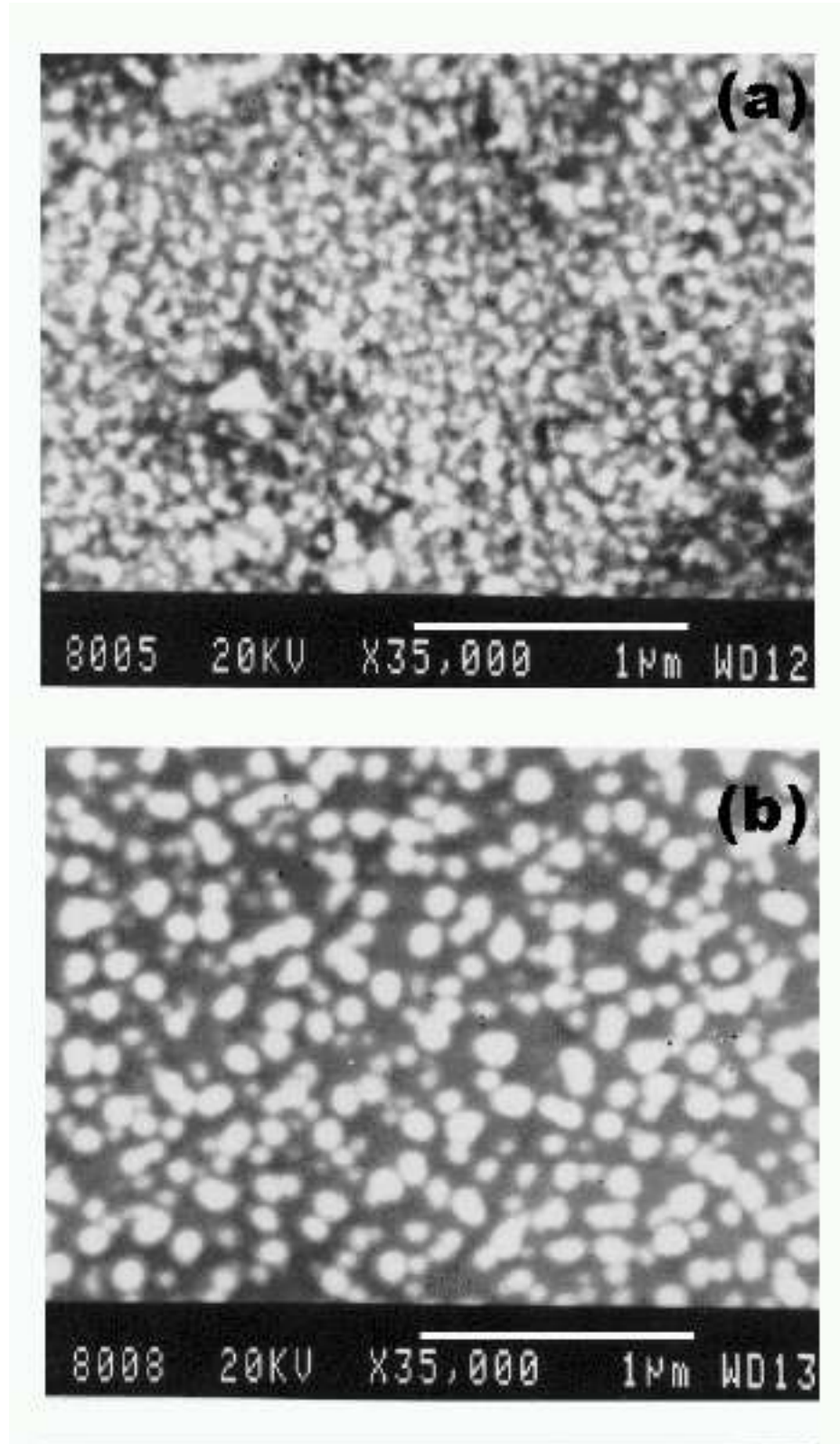


FIG. 4: SEM micrographs of two films with different thickness (a) 130nm and (b) 380nm, showing grains with voids between neighbouring grains. It is evident that as grain size increases the voids also increase.

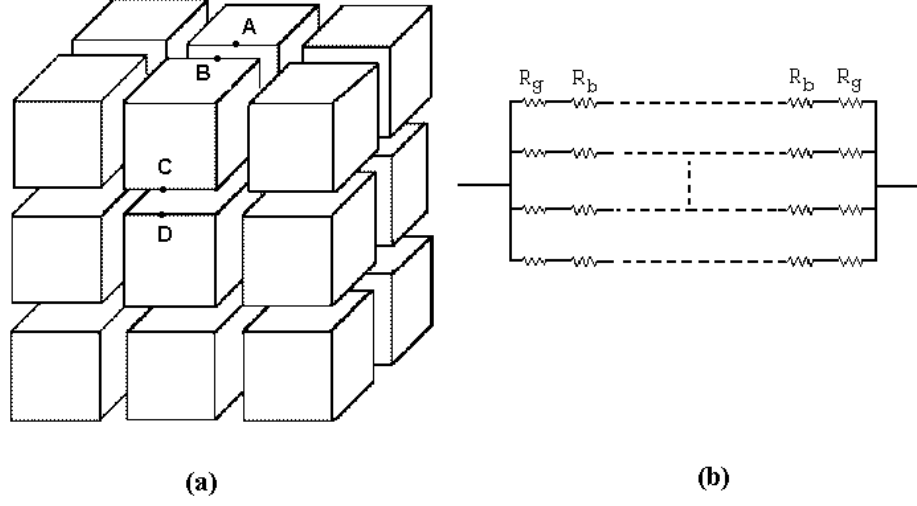


FIG. 5: Figure shows (a) an idealised assumption of how cubic grains are arranged along the dimensions of a polycrystalline film and (b) shows an equivalent circuit of the a polycrystalline film based on simplified assumptions.

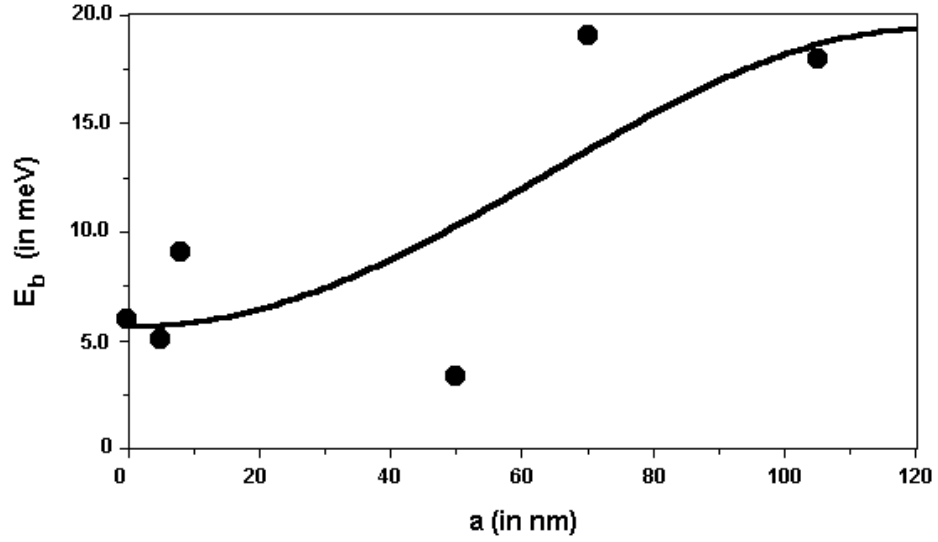


FIG. 6: Plot shows the variation of energy barrier height with improving grain size. The continuous curve is a fit of the experimental point using Slater's model (equation 5). The scattered points indicate other influences also on the barrier height.

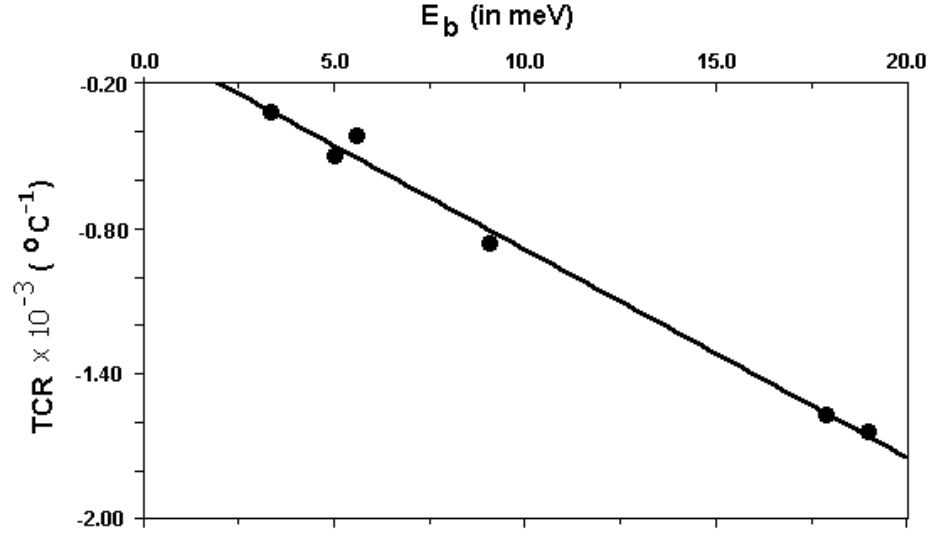


FIG. 7: The linear variation of temperature coefficient of resistance (TCR) with the barrier height implies the dependence of with the grain size.